Refractive Indices of the Inert Gases.

Element.	$\mu - 1$.	Observer.
Helium ………	$\frac{2 \cdot 84 \times 10^{27}}{40900 \times 10^{27} - n^2}$	Burton.
Helium ………	$\frac{2 \cdot 46 \times 10^{27}}{35500 \times 10^{27} - n^2}$	C. Cuthbertson and E. P. Metcalfe.
Neon …………	$\frac{5 \cdot 133 \times 10^{27}}{38517 \times 10^{27} - n^2}$	C. and M. Cuthbertson.
Argon …………	$\frac{9 \cdot 124 \times 10^{27}}{16335 \times 10^{27} - n^2}$	Burton.
Krypton ………	$\frac{10 \cdot 945 \times 10^{27}}{13039 \times 10^{27} - n^2}$	C. and M. Cuthbertson.
Xenon…………	$\frac{12 \cdot 47 \times 10^{27}}{9140 \times 10^{27} - n^2}$	,, ,,

On the Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen, and their Relations.

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(Communicated by Prof. F. T. Trouton, F.R.S. Received September 24,—Read November 25, 1909.)

Though there have been many determinations of the dispersion of air, and a few of those of oxygen, nitrogen, and hydrogen, the degree of accuracy hitherto attained can hardly be called satisfactory. The figures given by careful observers are not concordant, and those who wish to make use of them in further research find little to guide them in choosing the best values.

This is our apology for undertaking new determinations, and for offering a brief summary and criticism of previous work.

The apparatus (Jamin's refractometer) and method were those previously described,* but two improvements were introduced. In measuring the dispersion of the inert gases we had balanced the retardation of light of specific wave-length by the gas against an equal retardation by air, and measured only the relative dispersion. But, in the case of air itself, absolute measurements were necessary. For this purpose a new form of compensator was devised,[*] and the refraction of the gas was balanced against that of glass of known refractive index. Having thus ascertained the dispersion approximately from a continuous spectrum as nearly monochromatic as could be obtained with white light, accurate measurements were made by a modification of a method used by Rentschler.[†]

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* C. Cuthbertson and E. P. Metcalfe, 'Roy. Soc. Proc.,' A, vol. 80, p. 411, 1908.

Four monochromatic wave-lengths were employed: 6563, 5790, 5461, and 4861. Having observed the initial position of the bands for light of these wave-lengths, a large number of bands (400, 600, or 800) were counted in the green ($\lambda = 5461$), and the final relative positions of the bands of different wave-lengths were again observed. When the order of magnitude of the dispersion is approximately known, there is no difficulty in selecting the correct whole number of bands to be added to each fraction observed.

For example, if 800 bands of wave-length 5460·7 have been counted, the corresponding number of bands of wave-length 6563·042, which would have passed if there had been no dispersion, would be 665·64, and if the fraction of a red band actually observed is 0·76, we know that the number of bands due to dispersion is 665·64 − (an integer + 0·76) = an integer + 0·88. The second integer is found to be 4: and the value obtained by using this figure is the only one which agrees approximately with previous determinations. The use of 3 or 5 would give a dispersive power 20 per cent. too low or high.

AIR.

In expressing the dispersion of air, nearly everyone has made use of Cauchy's formula $\mu - 1 = a(1 + b/\lambda^2)$, generally subject to the reserve that no theoretical importance is to be attached to it. We shall, therefore, employ it in the first instance for the expression of our results, and shall then point out its inadequacy for future work.

Since the composition of air is not constant, it is useless to spend time in determining the absolute index of a particular sample to a high degree of accuracy. It is enough to state that the mean of five careful determinations of specimens of air from the neighbourhood of Gower Street, London, W.C., dried over phosphorus pentoxide, but not deprived of carbonic acid, gave, for the green mercury line, a refractive index of 1·0002936. These experiments were made at the temperature of the room and between the pressures 0 and 760 mm., and were reduced to n.t.p. by the formula

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[*] The compensator of Jamin is not suitable for measuring dispersion, since the path retardation for different wave-lengths is not the same. The new form consists of four wedges of glass, arranged in pairs so as to be equivalent to two plane parallel plates, and interposed at right angles to the beam. By screwing one of the wedges up or down the path retardation of one beam could be altered. The dispersion of the glass was measured by a prism, and checked by the interference method to be described.

[†] Rentschler, 'Astrophysical Journal,' December, 1908, p. 345.

$$\nu-1 = (\mu-1)\frac{760}{\mathrm{P}}\times\frac{t}{273},$$

where $\mu-1$ is the observed refractivity, and $\nu-1$ the value under standard conditions.

Starting from this value the relative retardations at the points $\lambda = 6563$, 5790, and 4861 were obtained by using as sources of light a hydrogen vacuum tube and a Bastian mercury light.

From six experiments the following values were found for the refractive indices of air for the wave-lengths given in the first column :—

$\lambda \times 10^8$.	$(\mu-1)10^6$.
6563	291·92
5790	292·98
5461	293·60
4861	295·11

In each experiment the values of b in Cauchy's formula were calculated from the observations for each section of the spectrum 6563—5790, 5790—5461, 5461—4861, and for the whole range 6563—4861. The following values were found :—

Table I.—Dispersion of Air.

Values of $b\times 10^{11}$ in Cauchy's formula $\mu-1 = a\left(1+\frac{b}{\lambda^2}\right)$.

Experiment.	λ = 6563—5790.	λ = 5790—5461.	λ = 5461—4861.	λ = 6563—4861.	Number of bands counted.
1	5·57	5·82	5·74	5·69	400
2	5·6	5·89	6·01	5·90	600
3	5·67	5·82	5·95	5·84	800
4	5·62	5·62	6·05	5·81	400
5	5·55	5·75	5·99	5·8	400
6	5·67	5·78	5·80	5·77	400
7	—	—	—	5·79	300
Mean...	5·61	5·78	5·98	5·80	—

If these figures are not so concordant as might be wished it must be remembered that the quantities measured are extremely small, and that the middle section $\lambda = 5790$ to $\lambda = 5461$ is a narrow one. For example, if 400 bands of wave-length 5461 have been counted, the relative retardation of light of wave-length 5790 is only 0·8 of a band, and it is not possible to read the bands to less than one-twentieth. We think, however, that the persistence with which the values of b increase as we pass from red to violet indicates a real change, and not the influence of an undetected source of error, and we believe the arithmetical means given in the last row are not far from the truth. This conclusion is supported by the fact that a similar variation is shown by every gas in which our dispersion measurements are sufficiently accurate, and by many of the observations of others. Such a result was to be expected from theoretical considerations, and from the experimental results of Kayser and Runge for the ultra-violet; but, so far as we know, it has not yet been accepted as proved for the visible spectrum. Previous workers, such as Jamin, Mascart, and Perreau have recorded different values for b for different parts of the spectrum; but it will be seen below that their observations have not the continuity which we have a right to expect in the dispersion of a colourless gas.

If two terms of Cauchy's formula are insufficient, the next step must be the addition of a term involving $1/\lambda^4$.

From the values given above for 6563, 5790, and 4861 we obtain the formula

$$\mu - 1 = 0{\cdot}00028854 + \frac{13{\cdot}38}{\lambda^2 10^{15}} + \frac{5{\cdot}0}{\lambda^4 10^{24}}$$

$$= 0{\cdot}00028854\left(1 + \frac{4{\cdot}636}{\lambda^2 10^{11}} + \frac{1{\cdot}73}{\lambda^4 10^{20}}\right).$$

The first of these expressions bears a close resemblance to that of Kayser and Runge, who, working in the blue and ultra-violet between $\lambda = 5630$ and $\lambda = 2360$, found

$$\mu - 1 = 0{\cdot}00028817 + \frac{13{\cdot}16}{\lambda^2 10^{15}} + \frac{3{\cdot}1600}{\lambda^4 10^{24}}.$$

In comparing these formulæ it is useful to remember that, in the visible spectrum, the contribution of the second term to the total is about ten times that of the third.

It is, however, more interesting to express the dispersion in terms of the formula

$$\mu - 1 = \frac{C}{n_0^2 - n^2}, \tag{1}$$

where n_0 is the frequency of the free vibration (assuming one only to be preponderant). From the first and third of the absolute values above we find $\mu_\infty - 1 = 0{\cdot}00028803$; and from the second and fourth 0·00028820. Taking the mean 0·00028812, we obtain the following values for n_0^2, λ_0^2 and λ_0, by using the wave-lengths given in column 1 respectively:—

$\lambda \times 10^8$.	$n_0^2 \times 10^{-27}$.	$\lambda_0^2 \times 10^{15}$.	$\lambda_0 \times 10^8$.
6563	16051	56069	748·79
5790	16183	55610	745·72
5461	16170	55658	746·04
4861	16100	55902	747·67
Mean......	16125	55810	747·05

whence

$$\mu - 1 = \frac{4{\cdot}6463 \times 10^{27}}{16125 \times 10^{27} - n^2}.$$

The values for the indices given by this formula are compared below with the experimental values—

$\lambda \times 10^8$.	$(\mu - 1) \times 10^7$.	
	Observed.	Calculated.
6563	2919·2	2919·03
5790	2929·8	2929·97
5461	2936·0	2936·16
4861	2951·1	2950·90

The differences between the observed and calculated numbers are well within the limits of error of experiment, and justify the use of this formula.

PREVIOUS MEASUREMENTS.

We may now turn to the results of previous observers and compare their figures and methods.

Ketteler,* using Jamin's apparatus, counted the number of red and green bands which corresponded to a known number of yellow bands. He obtained the numbers shown in the second column below—

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* Ketteler, 'Pog. Ann.,' vol. 124, pp. 390—406, 1865, and 'Farbenzerstreuung der Gase,' Bonn, 1865. The limitations of his range of observation were evidently imposed by the difficulty of obtaining adequate sources of monochromatic light. He used the lithium, sodium, and thallium flame spectra.

$\lambda \times 10^8$.	$(\mu-1)10^6$.	$b \times 10^{11}$.	
		Ketteler.	Present determination.
6708	293·87	5·36	5·47
5894·6	294·90	5·79	5·67
5350·5	295·94		

In the third column are given the values of b in Cauchy's formula, calculated from Ketteler's figures between each pair of limits, and in the last the corresponding values from the present determination. It will be remarked that the increase in b found by Ketteler is well marked, but is more rapid than we find it. The difference between his value for $\mu - 1$ for $\lambda = 6708$ and $\lambda = 5350{\cdot}5$, *i.e.* the dispersive power, is exactly the same as that found by us.

Lorenz* worked with a similar apparatus, but used only two rays, $\lambda = 6708$ and D_1D_2. He obtained—

$\lambda \times 10^8$.	$(\mu-1)10^6$.	$b \times 10^{11}$.
6708	290·06	5·41
5594·6	291·1	

This value is midway between that of Ketteler and the present determination. Lorenz deprived his air of moisture and CO_2.

Mascart used Talbot's bands, and chose as fixed points the wave-lengths $D = 5888$ and four lines in the cadmium spectrum, 6438, 5379, 5086 and 4799. He usually counted only 300 bands, and measured the dispersion between D and each of the other lines in turn. He thus obtained the following values, with which he was "entirely satisfied, considering the number of factors and the smallness of the quantities measured":—†

Between λλ.	Mascart.	Corrected.
6438—5888	5·0	4·9
5888—5379	6·2	6·3
5888—5086	5·9	6·0
5888—4799	6·0	6·1
Mean ……	5·8	5·81

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* L. Lorenz, 'Ann. der Phys. und Chem.,' N.F. 11, p. 70, 1880.

† Mascart, 'Ann. de l'Ec. Normale Supérieure,' 1877, p. 1.

It will be observed that the last three values are not independent of each other, so that their agreement is not so satisfactory as it looks. The mean for the whole spectrum is in accordance with those of other observers, but the difference between the first and second values is suspiciously great. However, looking to the fact that the whole effect observed was not more than half a band, and that Mascart did not claim to read to less than one-tenth of a band, a higher degree of accuracy was not to be expected. Had Mascart used the more accurate values for these wave-lengths which are now available, he would have obtained the numbers given in the third column above, which are not very different from his own.

Kayser and Runge* interposed a hollow glass prism over the lower half of a spectrum formed by a concave Rowland grating, and measured the change of position of standard lines due to change of air pressure in the prism. They worked between $\lambda = 5630$ and $\lambda = 2360$, and their pressure change was as high as 10 atmospheres.

Their formula for dry air is

$$\mu-1 = 0{\cdot}00028817+\frac{1{\cdot}316}{\lambda^2 10^{14}}+\frac{3{\cdot}16}{\lambda^2 10^{24}}.$$

The concordance between this result and that which we obtain for the visible spectrum has been mentioned.

Perreau† used the actual tubes of Mascart under his supervision, but discarded Talbot's bands, and obtained a banded spectrum by analysing white light which had passed through a Jamin refractometer. Following Mascart, he measured the dispersion between D_1 and each of the cadmium lines. He counted as many as 1500 bands, and also used the method of counting a small number of bands, and then estimating a large number from the ratio of the two pressure changes.

His values are as follows :—

$\lambda \times 10^8$.			$b \times 10^{11}$.
Between	6438	and 5896	6·3
	5378		5·3
	5085		5·5
	4800		5·8
	4677		5·4
		Mean.........	5·6

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* Kayser and Runge, 'Wied. Ann.,' vol. 50, p. 293, 1893.

† Perreau, 'Ann. de Ch. et de Physique,' vol. 7, p. 289, 1896.

Perreau is the only observer who finds a larger value for b in the red than in the rest of the spectrum, and he records the same phenomenon in about the same proportions in the dispersion of hydrogen, carbon monoxide, and carbon dioxide. This circumstance suggests the possibility that some undiscovered source of error underlay his method. His mean value for the whole spectrum is slightly lower than that of others, and the method of obtaining it, by taking the arithmetic mean of overlapping observations, is open to criticism. It is to be observed, however, that three of his observations show increasing values of b as we approach the violet.

Scheel* used an apparatus designed to measure the coefficient of expansion of quartz and platinum. He used Fizeau's bands, and the length of his cylinder containing air was only 1·46 cm., giving an effective length of 2·92 cm., which is altogether inadequate to give accurate results for dispersion. He could not have read more than 12 bands in the red per atmosphere of pressure. He worked between $\lambda = 7056$ and $\lambda = 4358$, and gives as a result

$$(\mu-1)\,10^7 = 2870{\cdot}5\left(1+\frac{5{\cdot}67}{\lambda^2 10^{11}}\right).$$

He appears to have made only two experiments, and the want of concordance between the readings is noticeable. He used air, dried, but not deprived of CO_2.

Rentschler† has recently published an investigation of the blue and ultra-violet dispersion between $\lambda = 5791$ and $\lambda = 3341$. He used a Fabry and Perôt *étalon*, the distance between his plates being 0·78 cm., so that he could not have read more than eight bands for a pressure difference of one atmosphere.

This deficiency is only partially compensated by the increased sharpness of the bands. His points of reference were three pairs of neighbouring lines, and his curve is plotted from the means of the values for the two numbers of each pair. He gives

$$\mu-1 = 0{\cdot}0002903+\frac{3{\cdot}80}{\lambda^2 10^{15}}+\frac{1{\cdot}23}{\lambda^4 10^{23}}.$$

The calculation by which he reduced his observations is not given. His curve is flatter than that of Kayser and Runge in the red and steeper in the violet, and the high value for infinite wave-lengths is unique. If, from his value for $\lambda = 5461$, we calculate b in Cauchy's formula, we find $2{\cdot}76 \times 10^{-11}$, which is improbable.

From this brief review it appears that there is a general agreement that the value of b is $5{\cdot}8 \times 10^{-11}$, between the red and violet, and a strong case for a rise in its value as λ decreases. It would also appear that the accuracy of a determination is not a function of its date.

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* Scheel, 'Ber. der Deut. phys. Gesell.,' p. 3, 1907.

† Rentschler, 'Astrophysical Journal,' December, 1908, p. 345.

OXYGEN.

The existing determinations of the dispersion of oxygen are only three in number. Lorenz' values for the red and yellow, reduced to Cauchy's formula, give

$$\mu - 1 = 0{\cdot}00026624\left(1 + \frac{6{\cdot}75}{\lambda^2 10^{11}}\right).$$

Mascart gives for b the values—

Between $\lambda\lambda \times 10^8$.	$b \times 10^{11}$.
6437—5888	4·9
5888—5377	7·8
5888—5084	6·4

figures which are very discrepant.

Rentschler has

$$(\mu - 1)\,10^7 = 2697{\cdot}4 + \frac{3{\cdot}72}{\lambda^2 \times 10^8} + \frac{1{\cdot}26}{\lambda^4 \times 10^{16}},$$

a formula in which the coefficients of λ^2 and λ^4 are nearly identical with those he gives for air, but slightly less.

Our oxygen was prepared by electrolysis of pure potassium hydroxide, freed from ozone, and deprived of moisture. For the green mercury line we found $\mu - 1 = 0{\cdot}0002717$, and, assuming this value, the following values were found for the refractive indices for the wave-lengths given in the first column, as the mean of five experiments:—

$\lambda \times 10^8$.	$(\mu - 1)\,10^6$.
6563	269·75
5790	270·99
5461	271·70
4861	273·45

The following table shows the values of b in Cauchy's formula, calculated from the figures of each experiment, and it will be observed that, as in the case of air, the values of b increase as we pass from red to violet:—

Table II.—Dispersion of Oxygen.

Values of $b \times 10^{11}$ in Cauchy's formula, $\mu - 1 = a\left(1 + \frac{b}{\lambda^2}\right)$.

Experiment.	$\lambda\lambda \times 10^8$.				Number of bands counted.
	6563—5790.	5790—5461.	5461—4861.	6563—4861.	
1	7·01	7·20	7·42	7·22	450
2	6·95	7·38	7·55	7·31	800
3	7·17	6·88	7·8	7·43	450
4	7·15	7·11	7·59	7·35	470
5	7·12	7·17	7·59	7·35	800
Mean......	7·08	7·215	7·54	7·33	

The second and third sections of the third experiment are obviously vitiated and are neglected in the mean.

If we use the value $b = 7{\cdot}33$, the dispersion of oxygen can be expressed by the formula

$$\mu - 1 = 0{\cdot}00026509\left(1 + \frac{7{\cdot}33}{\lambda^2 10^{11}}\right).$$

But if the formula (1), p. 154, is employed, our experimental results work out as follows:—

From the values for $\lambda = 6563$ and $\lambda = 5460$, $\mu_\infty - 1 = 0{\cdot}00026537$

" " $\lambda = 5790$ " $\lambda = 4861$, $\mu_\infty - 1 = 0{\cdot}00026528$

Mean .... 0·00026532

whence we derive the following values of the constants by using the wave-lengths given in column 1:—

$\lambda \times 10^8$.	$n_0^2 \times 10^{-27}$.	$\lambda_0^2 \times 10^{15}$.	$\lambda_0 \times 10^8$.
6563	12,723	70,737	841·05
5790	12,830	70,143	837·51
5461	12,852	70,022	836·79
4861	12,808	70,266	838·25
Arithmetical means	12,804	70,292	838·4

This leads to the formula for oxygen (O_2)—

$$\mu - 1 = \frac{3{\cdot}397 \times 10^{27}}{12804 \times 10^{27} - n^2}.$$

NITROGEN.

There have been three determinations of the dispersion of nitrogen. Mascart found the following values for b:—

Between $\lambda\lambda \times 10^8$.	$b \times 10^{11}$.
6563—5888	5·2
5888—5377	7·6
5888—5084	7·3
Mean	6·7

He points out, however, that there must be something wrong with his results, since the values he finds of b for oxygen and nitrogen are both greater than for air.

Scheel gives $(\mu-1)\,10^7 = 2906{\cdot}1\left(1+\frac{7{\cdot}732}{\lambda^2 10^{11}}\right)$.

Rentschler has

$$(\mu-1)\times 10^7 = 2941+\frac{3{\cdot}81}{\lambda^2 10^8}+\frac{1{\cdot}21}{\lambda^4 10^{16}},$$

which is liable to the same criticism as his results for air. These are the only previous attempts we can find recorded.

Our nitrogen was prepared by heating pure potassium nitrite with ammonium chloride; and was passed over potassium hydroxide, sulphuric acid, and phosphorus pentoxide. For the green mercury line we found, as the mean of seven experiments, $\mu-1 = 0{\cdot}00029977$. Assuming this value, the following values of the refractive index were found, for the wave-lengths given in column 1, from six experiments:—

λ.	$(\mu-1)\,10^6$.
6563	298·16
5461	299·77
4861	301·21

The following table shows the values of b in Cauchy's formula, calculated from the figures of each experiment, as in the case of air, except that the spectrum is divided into two sections, instead of three, owing to the smallness of the quantities observed:—

Table III.—Dispersion of Nitrogen.

Values for $b\times10^{11}$ in Cauchy's formula, $\mu-1 = a\left(1+\frac{b}{\lambda^2}\right)$.

λλ 6563—5461.	λλ 5461—4861.	λλ 6563—4861.	No. of bands counted.
5·30	5·67	5·54	400
5·45	5·55	5·498	800
5·50	5·67	5·57	400
5·40	5·60	5·50	800
5·19	5·68	5·42	400
5·275	5·67	5·47	800
Mean...... 5·36	5·63	5·496	—

Again we observe the rise in b between the red and violet.

Using the value $b = 5{\cdot}496$, the dispersion of nitrogen may be expressed in Cauchy's formula thus—

$$\mu-1 = 0{\cdot}00029434\left(1+\frac{5{\cdot}496}{\lambda^2 10^{11}}\right);$$

but using the formula (1) on p. 154, we obtain

From the values for 6563 and 5461, $\mu_\infty-1 = 0{\cdot}0002946$
„ „ 5461 „ 4861, $\mu_\infty-1 = 0{\cdot}00029439$
Mean .... $0{\cdot}00029450$

Whence n_0^2, λ_0^2, and λ_0 are found from each of the three wave-lengths in the first column.

Calculated from $\lambda\times10^8$.	$n_0^2\times10^{-27}$.	$\lambda_0^2\times10^{15}$.	$\lambda_0\times10^8$.
6563	17,022	52,873	724·0
5461	17,168	52,423	727·1
4861	17,094	52,650	725·6
Arithmetical means...	17,095	52,649	725·6

And the formula for nitrogen (N_2) becomes

$$\mu-1 = \frac{5{\cdot}0345\times10^{27}}{17095\times10^{27}-n^2}.$$

A good verification of these results can be found in comparing the refractivity of air with the sum of the refractivities of its constituents multiplied by the proportions in which they occur; and verification is the more desirable because the value obtained for the dispersive power of nitrogen is widely different from those previously recorded. In 100 c.c. of atmospheric air there are, approximately, 20·84 of oxygen, 78·22 of nitrogen, and 0·94 of argon. The quantities of carbon dioxide and ammonia may be neglected. Using Burton's determination of the refractivity of argon, our figures work out as follows:—

Table IV.—Comparison of the Refractivity of Air and its Constituents.

	$(\mu-1)\times 10^7$.		
	Observed, $\lambda = 5461$.	Calculated for $\lambda = \infty$.	
		Cauchy's formula of two terms.	Lorentz's formula.
Refractivity of air	2936	2881 ·7	2881 ·2
Sum of refractivities of constituents	2937 ·8	2880 ·99	2882 ·4

The correspondence between the figures in the first column shows the degree of accuracy attained in measuring the absolute refractivities; while those in the second and third show that the values found for the dispersive power are not far wrong.

The same test may be more simply applied in the following way: It is plain that if the dispersive power of nitrogen and oxygen are different from that of air, the excess of the one over that of air should equal the defect of the other; or to a first approximation,

$$(a_A b_A - a_N b_N)\times 79 = 21\,(a_O b_O - a_A b_A),$$

where a_A, a_N, a_O, b_A, b_N, b_O are constants of Cauchy's formula for air, nitrogen, and oxygen. Substituting the values given above, the left-hand side = 44, and the right-hand side = 57; the difference is equivalent to an error of 1 per cent. in the value of b for nitrogen, or of 3·4 per cent. in the value of b for oxygen, assuming the value for air.

HYDROGEN.

For this gas Ketteler found—

$\lambda\times 10^8$.	$(\mu-1)\times 10^6$.	$b\times 10^{11}$.
6870	142 ·17	7 ·2
5894	142 ·94	7 ·37
43079	145 ·54	

figures which lead to the values for b given in the third column. L. Lorenz found between $\lambda = 6708$ and $\lambda = 5894$ the value $b = 7{\cdot}63$. Mascart and Perreau's results may be expressed in the same table—

Between $\lambda\lambda \times 10^8$.	$b \times 10^{11}$.	
	Perreau.	Mascart.
6438—5896	8·5	3·8
5896—5378	7·4	4·0
5896—5085	7·7	5·1
5896—4800	7·9	
5896—4677	7·8	
Mean.........	7·8	4·3

Scheel gives
$$(\mu - 1)\,10^7 = 1358{\cdot}3\left(1 + \frac{6{\cdot}68}{\lambda^2 10^{11}}\right).$$

It will be seen that these results are not very concordant. Perreau accounts for the discrepancy between his results and those of Mascart by alleging that Mascart did not count enough bands. Scheel probably only counted six or seven bands in the red.

Our hydrogen was first prepared by electrolysis and then purified by absorption by palladium. For the line $\lambda = 5460{\cdot}7$ we find $\mu - 1 = 0{\cdot}00013971$. Assuming this value, the refractive indices for the wave-lengths given in the first column were found experimentally to be—

λ.	$(\mu - 1)\,10^6$.
6563	138·66
5790	139·33
5461	139·71
4861	140·64

The following table shows the value of b in Cauchy's formula, calculated from the figures of each experiment, as in the case of air :—

Table V.—Dispersion of Hydrogen.

Values of $b \times 10^{11}$ in Cauchy's formula, $\mu - 1 = a\left(1+\frac{b}{\lambda^2}\right)$.

λλ × 10^8.				
6563—5790.	5790—5461.	5461—4861.	6563—4861.	No. of bands counted.
[7·12]	[8·02]	—	7·50	279
7·45	7·62	7·87	7·65	400
7·48	7·87	7·90	7·72	450
7·48	7·5	7·67	7·60	450
7·50	7·2	7·69	7·57	450
Means ...... 7·477	7·55	7·78	7·61	—

Here, again, we notice the gradual rise of *b* between red and violet. If we use the value 7·61 the dispersion of hydrogen can be expressed by the formula

$$\mu - 1 = 0{\cdot}00013623\left(1+\frac{7{\cdot}61}{\lambda^2 10^{11}}\right);$$

but using the formula (1) on p. 154, we obtain—

From the values for $\lambda = 6563$ and 5461, $\mu_\infty - 1 = 0{\cdot}00013634$

" " $\lambda = 5790$ " 4861, $\mu_\infty - 1 = 0{\cdot}00013630$

Mean .... 0·00013632

whence we derive the following values of the constants calculated from the wave-lengths given in the first column respectively.

$\lambda \times 10^8$.	$n_0^2 \times 10^{-27}$.	$\lambda_0^2 \times 10^{15}$.	$\lambda_0 \times 10^8$.
6563	12,392	72,629	852·2
5790	12,424	72,436	851·1
5461	12,431	72,400	850·9
4861	12,391	72,630	852·3
Arithmetical means...	12,409	72,524	851·6

This leads to the formula for hydrogen (H_2),

$$\mu - 1 = \frac{1{\cdot}692 \times 10^{27}}{12409 \times 10^{27} - n^2}.$$

RELATION BETWEEN THE REFRACTIVITIES OF HYDROGEN, OXYGEN, AND NITROGEN.

In 1904, Drude* further developed his theory of dispersion in such a way as to calculate the sum of the valencies contained in the molecule of a compound, and obtained numbers which in some cases agreed with, and in others differed from, the accepted chemical valencies. His paper deals principally with the liquid and solid states, and he notes that, of gaseous elements, hydrogen alone has approximately the same number of valencies as in compounds (p. 719).

In his paper on the electromagnetic theory of dispersion and extinction,† Natanson has collected a number of experimental results for the refraction and dispersion of gaseous elements and compounds, and shows that when these are averaged there is a first approximation to constancy in the product $v \times 3\pi c^2 m/e^2 N$, where v is the valency, for hydrogen, oxygen, air, carbon monoxide, carbon dioxide, ammonia, carbon disulphide, and sulphurous oxide; but that nitrogen and compounds containing nitrogen departed from this rule. It was therefore with interest that the experimental results recorded above were submitted to this test.

The formula we have employed is in the form $\mu - 1 = C/(n_0^2 - n^2)$, where n_0 and n are respectively the frequencies of the free vibrations which are instrumental in effecting refraction and that of the incident light, and $n\lambda = V$. On Drude's theory the numerator of this expression is proportional to the number of electrons in unit volume of the medium. If this number is proportional to the positive valency of the atom, as Drude proposes, we should find C/V constant, where v is the valency.

The following table shows the application of this test:—

Element.	$\mu - 1$.	C.	V.	$\frac{C}{V} \times 10^{-27}$.
Hydrogen	$\frac{1 \cdot 692 \times 10^{27}}{12409 \times 10^{27} - n^2}$	$1 \cdot 692 \times 10^{27}$	1	1·692
Oxygen	$\frac{3 \cdot 397 \times 10^{27}}{12804 \times 10^{27} - n^2}$	$3 \cdot 397 \times 10^{27}$	2	1·699
Nitrogen	$\frac{5 \cdot 0345 \times 10^{27}}{17095 \times 10^{27} - n^2}$	$5 \cdot 0345 \times 10^{27}$	3	1·678

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* Drude, 'Ann. d. Physik u. Chem.,' vol. 14, p. 677, 1904.

† Natanson, 'Bull. de l'Acad. des Sc. de Cracovie,' April, 1907, p. 316.

The agreement is close. If our results should be confirmed by further work there would be little doubt that, in the case of these three elements, the number of "dispersion electrons" is proportional to the received valency.

By using the experimental results recorded in a previous paper by one of us, working with Mr. E. P. Metcalfe,* the comparison can be extended to the cases of phosphorus, sulphur, and mercury. For phosphorus the figures given were—

	$\lambda \times 10^8$.	$(\mu-1)\,10^6$.
1	6800	1200
2	5893	1212
3	5100	1230

from which was deduced the formula—

$$\mu-1 = 0{\cdot}001162\left(1+\frac{15{\cdot}3}{\lambda^2 10^{11}}\right).$$

Reducing these results to the form of Sellmeier's equation, we obtain from 1 and 2

$$\mu_\infty-1 = 0{\cdot}0011635,$$

and from 1 and 3 $\mu_\infty-1 = 0{\cdot}0011651,$

the mean of which is $0{\cdot}0011643,$

whence we find for $n_0{}^2 \times 10^{-27}$ from (1) 6542·4, from (2) 6582·8, from (3) 6478·0; mean 6534·4; and the equation becomes, for phosphorus (P_2),

$$\mu-1 = \frac{7{\cdot}61 \times 10^{27}}{6534 \times 10^{27}-n^2}.$$

On turning to the case of sulphur, we find that the figures published by Cuthbertson and Metcalfe were based on experiments with an unnecessarily small quantity of sulphur, and that the individual readings did not lead to very concordant values for $n_0{}^2$. We therefore attempted a redetermination of the dispersion. This, also, is not so accurate as we hope to make it, in the future, with improved apparatus and by spending more time and pains. But we believe it to be better than the former determination, from which it differs by about 5 per cent. The difficulties of the experiment are great, for the dispersion and absorption in the violet are so large that when 70 or 80 bands have passed, the bands disappear; and unless as many as this are read, the dispersion effect is less than one and a-half bands.

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* C. Cuthbertson and E. P. Metcalfe, 'Roy. Soc. Proc.,' A, vol. 80, p. 411, 1908.

Accepting the value for $\lambda = 5460{\cdot}7$ previously published, the refractivities in the red and green are now found to be—

	λ.	$(\mu-1)\,10^6$.
1	6900	1091·5
2	5461	1120·5
3	5086	1132·5

From 1 and 2 we find $n_0^2 = 4547 \times 10^{27}$,

„ 2 „ 3 „ $= 4653 \times 10^{27}$,

Mean, $46{,}000 \times 10^{27}$.

And this leads to the formula for sulphur (S_2)—

$$\mu - 1 = \frac{4{\cdot}808 \times 10^{27}}{4600 \times 10^{27} - n^2}.$$

On comparing these figures with those for oxygen and nitrogen given on p. 166, it appears that, on Drude's electronic theory, the number of "dispersion electrons" in an atom of phosphorus is $\frac{3}{2}$ times the number in an atom of nitrogen, and the number in an atom of sulphur is, with less exactness, $\frac{3}{2}$ times the number in an atom of oxygen.

From these figures the valency of phosphorus and sulphur can be deduced on the assumption that C/V is constant.

The following table shows the results:—

Element.	$\mu-1$.	C.	V.	$\frac{C}{V} \times 10^{-27}$.
Phosphorus	$\frac{7{\cdot}61 \times 10^{27}}{6534 \times 10^{27} - n^2}$	$7{\cdot}61 \times 10^{27}$	$4\frac{1}{2}$	1·691
Sulphur	$\frac{4{\cdot}808 \times 10^{27}}{4600 \times 10^{27} - n^2}$	$4{\cdot}808 \times 10^{27}$	3	1·603

The concordance with the results for hydrogen, oxygen, and nitrogen is quite as near as could be expected, considering the errors of experiment.

The deduction, that, if the valency of oxygen be taken as 2 that of sulphur is 3, or if oxygen is 4 sulphur is 6, is in accordance with expectation.

The deduction that the valency of phosphorus is $4\frac{1}{2}$ is surprising, for we do not think that the value is so erroneous that a better determination would give 5.

In the case of mercury, also, we find that the figures from which the dispersion formula was deduced in 1908 do not give very concordant values for n_0^2. The following table gives the values then chosen in the second column:—

$\lambda \times 10^8$.	$(\mu-1)\,10^6$.	$(\mu-1)\,10^6$ replotted.
6900	1840	
6800	—	1838
5893	1866	1866
5000	—	1906
4900	1920	

Replotting the old observations and smoothing the curve, we find that the values given in the third column are more probable, on the hypothesis, than an equation of Sellmeier's type should be adopted.

The old figures lead to the equation

$$\mu-1 = \frac{7{\cdot}82 \times 10^{27}}{4360 \times 10^{27} - n^2},$$

while the present revision gives

$$\mu-1 = \frac{8{\cdot}371 \times 10^{27}}{4740 \times 10^{27} - n^2}.$$

The number 7·82 corresponds to $4\frac{1}{2}$ dispersion electrons, and 8·731 corresponds to 5. Without laying too much stress on these values, we can draw the conclusion that the number of dispersion electrons is about five.

RATIO OF e/m AND VALUE OF e.

A dispersion equation of the type employed above, when based on the electronic theory, affords a means of calculating the ratio of the charge of a "dispersion electron" to the mass, or the amount of the charge. Mr. Norman Campbell,* using Ketteler's values of the dispersion of hydrogen, and the value $e/m = 5{\cdot}1 \times 10^{17}$ e.s.u. derived from the Zeeman effect finds that

$$\mathrm{N}e = 1{\cdot}74 \times 10^{10}.$$

Now if E is the charge on the hydrogen ion in electrolysis and N the number of atoms in 1 c.c. of gas,

$$\mathrm{NE} = 2{\cdot}45 \times 10^{10}.$$

Therefore

$$e/\mathrm{E} = 0{\cdot}7.$$

The values found by us differ considerably from those of Ketteler (who must have used impure hydrogen). Our figures are

$$\mu^2-1 = 2 \times \frac{1{\cdot}692 \times 10^{27}}{12409 \times 10^{27} - n^2},$$

since

$$\mu^2-1 = 2(\mu-1) \text{ for gases.}$$

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* See N. Campbell, 'Modern Electrical Theory,' p. 90.

Assuming
$$\mu^2-1 = \frac{Ne^2}{\pi m\,(n_0{}^2-n^2)},$$
we have
$$\frac{Ne^2}{2\,\pi m} = 1{\cdot}692\times10^{27};$$
and if
$$e/m = 5{\cdot}1\times10^{17},$$
then
$$Ne = \frac{1{\cdot}692\times10^{27}\times2\pi}{5{\cdot}1\times10^{17}} = 2{\cdot}09\times10^{10},$$
whence
$$e/E = 0{\cdot}85,$$
which is nearer to the expected value, unity.

Conversely, assuming that $e = E$, we would obtain
$$e/m = 4{\cdot}33\times10^{17}.$$

Summary.

The experimental results contained in this paper may be summarised as follows:—

1. In air, oxygen, nitrogen, and hydrogen it is found that Cauchy's formula of two terms $\mu-1 = a\,(1+b/\lambda^2)$ is inadequate to express the dispersion.[*] The values of b in this formula, calculated from the experimental results, increase in all cases as we pass from red to violet.

2. The dispersion of all these gases can be better expressed by a formula of the form used by Sellmeier and others, $\mu-1 = C/(n_0{}^2-n^2)$, where n_0 and n are the frequencies of the free vibration of the atom and of the incident light respectively.

3. The refractive indices of the gases in question are found to follow the laws—

	$\mu-1.$
Air	$\dfrac{4{\cdot}6463\times10^{27}}{16125\times10^{27}-n^2},$
Oxygen (O_2)	$\dfrac{3{\cdot}397\times10^{27}}{12804\times10^{27}-n^2},$
Nitrogen (N_2)	$\dfrac{5{\cdot}0345\times10^{27}}{17095\times10^{27}-n^2},$
Hydrogen (H_2)	$\dfrac{1{\cdot}692\times10^{27}}{12409\times10^{27}-n^2}.$

4. The refractive index of phosphorus, recalculated in the form of the same equation from previous observations, is
$$\frac{7{\cdot}61\times10^{27}}{6534\times10^{27}-n^2}.$$

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[*] In the preceding and following papers the same results are found for neon, sulphur dioxide, and hydrogen sulphide.

That of sulphur, redetermined, is

$$\frac{4 \cdot 808 \times 10^{27}}{4600 \times 10^{27} - n^2}.$$

That of mercury, recalculated from old observations re-examined, is about

$$\frac{7 \cdot 82 \times 10^{27}}{4360 \times 10^{27} - n^2} \text{ to } \frac{8 \cdot 37 \times 10^{27}}{4740 \times 10^{27} - n^2}.$$

On Drude's electronic theory, the numbers of "dispersion electrons" in hydrogen, oxygen, nitrogen, sulphur, and phosphorus are in the ratios of 1, 2, 3, 3, and $4\frac{1}{2}$ respectively.

With regard to the work recorded in this and the two connected papers, we have to express our great obligations to Prof. Trouton and Prof. Porter, of University College, London; also to the Royal Society for the assistance of a grant.

On the Refraction and Dispersion of Sulphur Dioxide and Hydrogen Sulphide, and their Relation to those of their Constituents.

By Clive Cuthbertson, Fellow of University College, London, and
Maude Cuthbertson.

(Communicated by Prof. F. T. Trouton, F.R.S. Received September 24,—Read November 25, 1909.)

Sulphur Dioxide.

The refractive index of sulphur dioxide for a single wave-length has been measured several times, and in a recent paper* it was shown that nearly all the values, when corrected for density, approximated to $\mu - 1 = 0 \cdot 000661$ for sodium light.

The dispersion has only been measured once, by Ketteler,† who found the numbers given in the second column below—

$\lambda \times 10^8$	$(\mu - 1) 10^6$.	$(\mu - 1) 10^6$, corrected for density
6707	681 ·54	656 ·7
5889	686 ·01	661 ·0
5350	690 ·71	665 ·5

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* C. Cuthbertson and E. P. Metcalfe, 'Roy. Soc. Proc.,' vol. 80, p. 406, 1908.

† Ketteler, 'Theoretische Optik,' p. 478, 1885.